CO-ASSIGNMENT OF THE MOLECULAR VIBRATIONAL FREQUENCIES IN DIFFERENT ELECTRONIC STATES

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Ultrafast electron diffraction experimental data for the structural parameters of molecules in excited electronic states are comparatively uncommon, hence these parameters are largely unknown. However, because differences between the molecular geometries of excited and ground electronic states cause differences in their experimental vibrational spectra it is important to establish a correspondence between the molecular vibrational frequencies in the ground state and those of the excited state of interest. The correct co-assignment of the experimental vibrational frequencies between two different electronic states of a molecule may be determined by the analog of the Duschinsky matrix[a] D. This matrix D is defined as $D = (L_{\mathrm{I}})^{-1} L_{\mathrm{II}}$ where L_{I} and L_{II} are the matrices of the vibrational modes of the two states of the molecule under investigation. They are obtained by solving the vibrational problems in the I and II electronic states, respectively. Choosing the dominant elements in columns of the D matrix and permuting these columns to arrange these elements along the diagonal of the transformed matrix D^* makes it possible to establish the correct co-assignment of the calculated frequencies in the two electronic states. The rows of D^* are for the vibrations in the I electronic state, whereas the columns are for vibrations in the II electronic state. The results obtained may be tested by analogous calculations of D^* for isotopologues. The feasibility of co-assignments of the vibrational frequencies in the ground and T_1 and S_1 excited electronic states are demonstrated for *trans*-$C_2O_2F_2$[b]. The analogs of the Duschinsky matrix D^* were used to juxtapose the vibrational frequencies of this molecule calculated at the CASPT2/cc-pVTZ level in the S_0, T_1 and S_1 states.

[a] F. Duschinsky, Acta Physicochim. URSS, 7(4), 551–566 (1937).
[b] Yu. N. Panchenko, Vibrational spectroscopy, 68, 236–240 (2013).